IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

#16
Declaration
FJONES
5-10-02

In re United States Patent Application of:			
Applicant:	**Peter C. Van Buskirk, et al.**	**Docket No.:**	**2771-337 RCE**
Application No.:	**09/200,495**	**Examiner:**	**S. Hu**
Date Filed:	**November 25, 1998**	**Art Group:**	**2811**
Title:	**OXIDATIVE TOP ELECTRODE DEPOSITION PROCESS AND MICROELECTRONIC DEVICE STRUCTURE**		

EXPRESS MAIL CERTIFICATE

I hereby certify that I am mailing the attached documents to the Commissioner for Patents on the date specified, in an envelope addressed to the Commissioner for Patents, Box AF, Washington, D.C., 20231 and Express Mailed under the provisions of 37 CFR 1.10.

Name of Person Mailing Document

Signature

Date

Express Mail Label Number

DECLARATION UNDER 37 CFR §1.131 IN U.S. PATENT APPLICATION NO. 09/200, 495

Commissioner for Patents
Box AF
Washington, D.C. 20231

Sir:

PETER C. VAN BUSKIRK, STEVEN M. BILODEAU, STEPHEN T. JOHNSTON, DANIEL J. VESTYCK and MICHAEL W. RUSSELL, severally and jointly hereby declare:

1. THAT we are co-inventors of the subject matter disclosed and claimed in United States Patent Application No. 09/200,495 filed November 25, 1998 in the United States Patent and Trademark Office in the names of Peter C. Van Buskirk, Steven M. Bilodeau, Stephen

T. Johnston, Daniel J. Vestyck, and Michael W. Russell and entitled, "OXIDATIVE TOP ELECTRODE DEPOSITION PROCESS, AND MICROELECTRONIC DEVICE STRUCTURE" hereafter referred to as the "Application."

2. THAT the Application discloses and claims a microelectronic device that comprise a bottom electrode, a top electrode and a ferroelectric or high ϵ film therebetween, wherein the ferroelectric or high ϵ film is stoichiometrically satisfied in oxygen content, and that the Application broadly claims such a system in the following claim 40:

> 40. (Twice amended) A microelectronic device structure including a top electrode layer on a top surface of a ferroelectric oxide or high ε oxide film material, wherein said ferroelectric oxide or high ε oxide film material is stoichiometrically satisfied in oxygen content, including the top surface region of the ferroelectric oxide or high ϵ oxide film material, and wherein the top electrode layer does not contain oxygen abstracted from the thin film of ferroelectric or high ϵ material underneath.

3. THAT we are aware that the Application has been examined by the United States Patent and Trademark Office, that we have read the February 5, 2002 Office Action issued by the United States Patent and Trademark Office, and that we are aware that the claims of the Application as originally filed have been rejected on various grounds including the disclosure of U.S. Patent 6,300,212 (Inoue, et al.) under 35 U.S.C. §102(e).

4. THAT we have been informed by our legal representatives that the rejection of the claims of the Application can be overcome by presenting evidence to the United States Patent and Trademark Office of our possession of our claimed invention prior to the effective date of the U.S. Patent identified in Paragraph 3, that said effective date has been identified to us by such legal representatives as July 29, 1998 (such date hereafter being referred to as "Effective Date").

5. THAT attached in Exhibit 1 hereof is a true and exact copy of pages 1-2 of an Invention Disclosure Document, on which all dates have been blacked out, but which dates are prior to the Effective Dates; that page 1 identifies co-inventors Peter C. Van Buskirk, Steven M. Bilodeau, Stephen T. Johnston, Daniel J. Vestyck, and Michael W. Russell, as writers of the document, and our assignee, ADVANCED TECHNOLOGY MATERIALS, INC., as

the project sponsor, that the title of the document is "[O]xidizing top electrode deposition process", that page 1, second last paragraph, discusses the need for preventing "the ferroelectric or high ϵ film from becoming oxygen deficient during TE deposition.", that page 2, discusses different methods for preventing oxygen deficiency in the ferroelectric film, including top electrode deposition techniques and PZT deposition techniques as described in the present specification Use of the disclosed methods of deposition provides for a microelectronic device wherein the ferroelectric or high ϵ film is not deficient of oxygen and stoichiometrically satisfied in oxygen content throughout.

6. THAT we offer Exhibit 1 with this Declaration as evidence of the completion and possession of the claimed methods of deposition and claimed microelectronic device having a ferroelectric or high ϵ film that is not deficient of oxygen and stoichiometrically complete in oxygen content throughout prior to the Effective Date identified in Paragraph 4 of this Declaration.

As a below-named declarant, I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements, and the like, so made are punishable by fine or imprisonment, or both, under Section 1001 or Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

PETER C. VAN BUSKIRK

STEVEN M. BILODEAU

STEPHEN T. JOHNSTON

DANIEL J. VESTYCK

MICHAEL W. RUSSELL

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PETER C. VAN BUSKIRK

STEVEN M. BILODEAU

STEPHEN T. JOHNSTON

DANIEL J. VESTYCK

04/24/02

MICHAEL W. RUSSELL

EXHIBIT 1

INVENTION DISCLOSURE

ROI Number [redacted]

Oxidizing top electrode deposition process

(1) State the PROBLEM or DEFICIENCY, which is overcome by your invention:

Ferroelectric and high ε thin films capacitors are becoming increasingly important in microelectronics, for use in advanced memories, as decoupling capacitors and infrared detectors, for example. The ferroelectric or high ε film is typically an oxide perovskite (or layered structure perovskite) such as $PbZrTiO_3$, $(Ba,Sr)TiO_3$ (or $SrBi_2Ta_2O_9$), although other similar materials are also used.

Properties of ferroelectric and high ε capacitors depend, in general, on the stoichiometry (atomic relative concentrations) of the film. Whilst the most common concern is the cation stoichiometry, film electrical properties are extremely sensitive to oxygen concentration as well.

Formation of the capacitor typically involves vacuum deposition of a metal on top of the oxide layer. It is likely that the top electrode (TE) deposition conditions will result in oxygen loss in the ferroelectric or high ε film, particularly at its surface. This oxygen loss may be due chemical or physical aspects of the TE deposition process. Chemical aspects include a higher affinity of O by the TE material (compared to the ferroelectric), or by another chemical driving force, such as the environment in a metal CVD process that may be used to deposit the TE. Physical effects include thermal desorption that could be stimulated by the transfer of energy of an incident atom, or by sputtering, whereby an adatom with superthermal energy (>1 eV) directly results in ejection of an O atom.

For dc magnetron sputtering of Ir (for example), adatom energies at the film surface can be on the order of 120 eV for Ar^1, and 25 eV for Ir. Since 200 eV Ar is known to modify the surface of crystalline Si to a depth of 28Å[2] it is plausible that Ar bombardment in a magnetron deposition process will have significant effects on the surface of a ferroelectric such as $PbZrTiO_3$.

While oxygen loss may in principle be compensated by post annealing in oxidizing conditions, this approach depends on the ability of the TE to allow O to diffuse from the annealing atmosphere to the ferroelectric film surface. Pt will allow O diffusion for that purpose, but other more desirable TE materials such as Ir and IrO_2 will not; they are good O diffusion barriers.

So a method is needed to prevent the ferroelectric or high ε film from becoming oxygen deficient during TE deposition.

(2) Describe clearly the INVENTION, RESULTS, ADVANTAGES. (Make DRAWINGS when possible and DESCRIBE FULLY the invention and its OPERATION using REFERENCE NUMERALS to indicate elements.

INVENTOR(S):

(Signature)	(Signature)	(Signature)	(Signature)	(Signature)
Peter Van Buskirk	Steve Bilodeau	Stephen Johnston	Dan Vestyck	Michael Russell
(Print Name)	(Print Name)	(Print Name)	(Print Name)	(Print Name)
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
(Date)	(Date)	(Date)	(Date)	(Date)

READ AND UNDERSTOOD BY:

Margaret Chappuis	
(Signature - Full Name)	(Signature - Full Name)
Margaret Chappuis	
(Print or Type Full Name)	(Print or Type Full Name)
[redacted]	
(Date)	(Date)

There are several ways to prevent oxygen deficiency in the ferroelectric film:

I. During TE deposition:

1. Sputter deposition of a metallic (non-oxide) TE in the presence of O. This method can use O_2, N_2O, NO_2, etc. for sputtering. Reactive sputtering with oxygen present is a well known way to deposit an oxide compound, but sputtering conditions such as pressure, substrate temperature and deposition rate can be often be adjusted to deposit a suboxide or pure metal even if oxygen is present. In those cases oxygen present in the working gas will tend to prevent a net loss of oxygen in the surface of the ferroelectric. Once the ferroelectric surface is covered, a different TE process can continue, with the oxygen source turned off for example. A pure metal TE may be desirable because it has a higher work function, which is known to reduce leakage in ferroelectric capacitors. Sputtered pure metal top electrodes often also have lower compressive stress than those sputtered in the presence of oxygen that may be desirable.

2. Evaporation of a noble metal in the presence of O, resulting in a metal TE, and a decreased tendency for the ferroelectric film to lose O during deposition. The rationale is the same as 1.

3. Minimize bombarding energy and flux during deposition by manipulating sputtering conditions, in order to minimize O loss from the surface, and to reduce physical damage to the lattice.

4. Process the ferroelectric surface so that it contains excess O, either in the lattice or in grain boundaries. This may be achieved by ion implantation of O at energies greater than 200 eV, either prior or subsequent to TE deposition.

5. Deposition of the noble metal TE (typically Ir or Pt or alloys containing those species) using a CVD process that incorporates oxygen, such as that described in the USP Applications by T. Baum et al., ATM-207/207D: "Platinum source compositions for CVD of Pt"

6. Deposition of a noble metal and an oxide compound mixed film, especially one that may "give up" its O easily, such as MnO, CeO_2, etc. In that way O may be provided to the ferroelectric surface without a long diffusion path through the metallic electrode.

II. During the PZT process

7. Terminate the PZT deposition process under oxygen-excess conditions.

8. Terminate the PZT deposition process under low oxygen conditions resulting in a "metallic capping" layer that may reduce oxygen mobility/depletion in the ferroelectric film. The "capping" layer can be etched in a pre-TE step under conditions that minimize surface depletion of oxygen thereby exposing the desired PZT film.

INVENTOR(S):

(Signature)	(Signature)	(Signature)	(Signature)	(Signature)
Peter Van Buskirk	Steve Bilodeau	Stephen Johnston	Dan Vestyck	Michael Russell
(Print Name)	(Print Name)	(Print Name)	(Print Name)	(Print Name)
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
(Date)	(Date)	(Date)	(Date)	(Date)

READ AND UNDERSTOOD BY:

(Signature - Full Name)	(Signature - Full Name)
Margaret Chappuis	
(Print or Type Full Name)	(Print or Type Full Name)
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(Date)	(Date)